

Semiconducting Delafossite Structures

David P. Cann

IOWA STATE UNIVERSITY

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- We have examined the role of non-stoichiometry in the electronic transport properties of $\text{Cu}_x\text{GaO}_{2+y}$ with an aim of elucidating the mechanism for the observed intrinsic *p*-type conductivity.
- As shown in Figs 1. (a)-(d), diffraction studies show clear trends in unit cell dimensions as a function on non-stoichiometry. Interestingly, these structural modifications were not correlated to any change in the conductivity:

$$\sigma_{300\text{ K}} \approx 0.01 (\Omega\text{-cm})^{-1}$$

- Fig. 2 displays *in situ* measurements of the resistivity during oxygen annealing that show a positive $d\rho/dt$ slope which correlates to the gradual decomposition of CuGaO_2 .
- The results of these studies make it clear that oxygen interstitials are not responsible for the observed *p*-type conductivity. The studies on the Cu/Ga stoichiometry indicate that the CuGaO_2 phase exhibits negligible equilibrium cation non-stoichiometry. This contrasts with non-equilibrium processing methods which may allow a greater degree of non-stoichiometry and thus an enhanced conductivity.
- Future work will explore the effects of co-doping on the electronic transport properties.

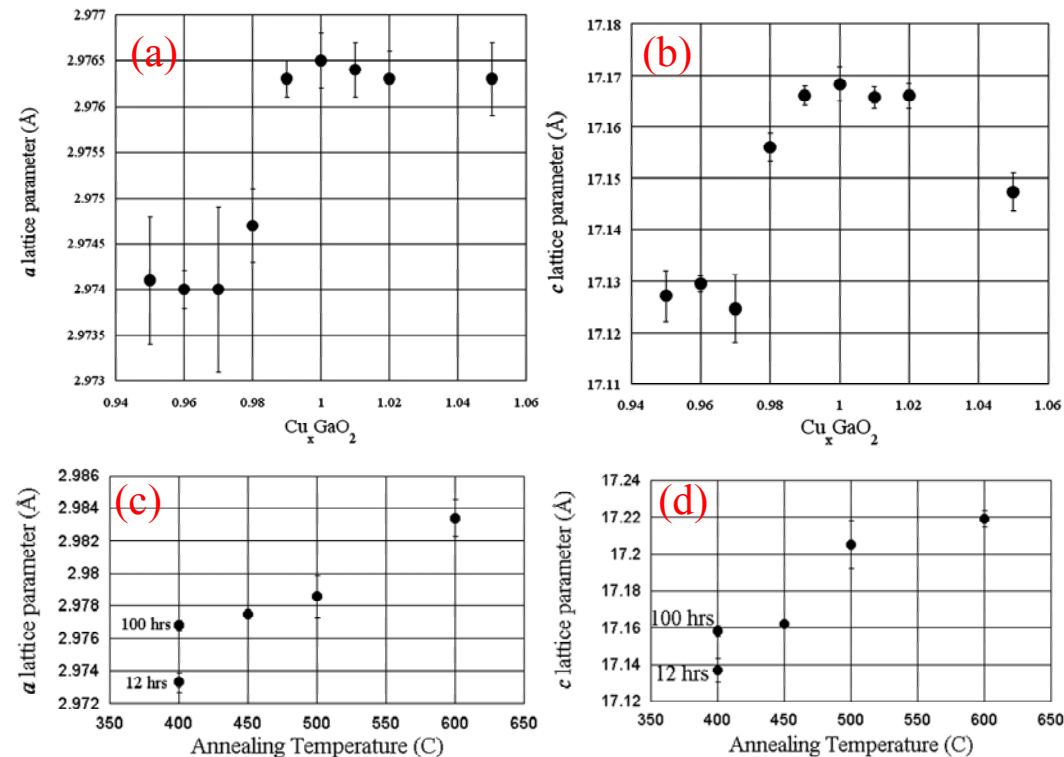
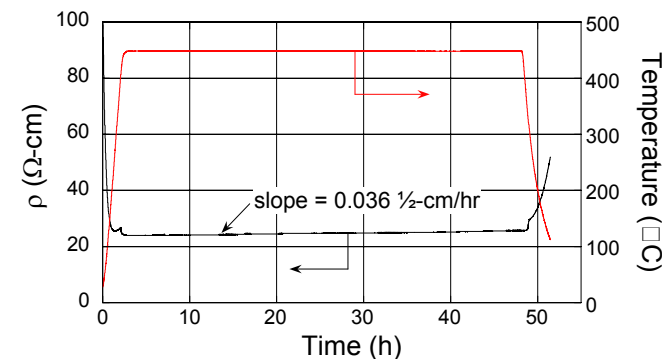


Fig. 1. Delafossite cell dimensions as a function of Cu concentration and O_2 annealing

Fig. 2. Resistivity as a function of time during O_2 annealing. The resistivity was measured *in-situ* during the temperature profile indicated on the graph.



Aim of the project:

Delafossite structures (ABO_2) have an unusual combination of materials properties including both transparency in the visible spectrum and bipolar semiconducting behavior. The objective of this work is to understand how the crystal chemistry and defect chemistry of the delafossite structure control the bipolar conductivity in compounds such as CuGaO_2 .

Research results:

In this work, we have examined the role of non-stoichiometry in the electronic transport properties of $\text{Cu}_x\text{GaO}_{2+y}$ with an aim of elucidating the mechanism for the observed intrinsic p -type conductivity. There are conflicting models in the literature for the dominant defect species in Cu-based delafossites. Drawing upon the known defect chemistry of Cu_2O , it has been suggested that Cu-vacancies and oxygen interstitials are the dominant defects. However, there have been no systematic studies of the influence of cation or anion stoichiometry on the conductivity. In many non-stoichiometric compounds, the defect equilibria can be established through measurement of the oxygen partial pressure dependence of the conductivity. However, because the delafossite structure is only stable over two or three decades in oxygen partial pressure it is difficult to make unambiguous conclusions from this approach. Therefore the focus of this study is to examine the limits of non-stoichiometry in CuGaO_2 through room temperature conductivity measurements of solid state synthesized compounds and relate the role of cation and anion point defects to the observed p -type conductivity.

As shown in Figs 1. (a)-(d), diffraction studies show clear trends in unit cell dimensions as a function on non-stoichiometry. Below a critical composition ($x=0.98$) the unit cell undergoes a contraction. Under O_2 anneals, the delafossite structure undergoes an isotropic expansion of approximately 1%. Interestingly, these structural modifications were not correlated to any change in the conductivity ($\sigma_{300\text{K}} \approx 0.01 \text{ S/cm}$, activation energy $E_A \approx 0.2 \text{ eV}$). The activation energy of 0.2 eV over the temperature range 200 – 500 K is indicative of small polaron conduction. This suggests that in essence CuGaO_2 is a line compound and that it is not possible to stabilize a significant degree of non-stoichiometry through equilibrium methods such as solid state synthesis.

Fig. 2 illustrates the time dependence of the resistivity via an *in situ* measurement during an oxygen anneal which followed the temperature profile indicated in the graph. As the temperature increased to 450°C, The sample exhibited a decrease in resistivity down to a minimum value of approximately 25 Ω -cm. During the isothermal hold, the sample exhibited a positive $d\rho/dt$ slope due to the decomposition of CuGaO_2 into the high resistivity phases CuO and CuGa_2O_4 .

Significance of this work:

The delafossite structure has unique transport properties (bipolarity, anisotropy) coupled with transparency in the visible spectrum. In particular, CuGaO_2 exhibits *p*-type conductivity in the absence of doping yet the mechanism for this *p*-type conductivity is unclear. From the results of this work on non-stoichiometric $\text{Cu}_x\text{GaO}_{2+y}$ compounds, it is possible to make some conclusions about the dominant defect species. From the results of the annealing studies it is clear that while lattice expansion is observed, the lack of an increase in conductivity suggests that oxygen interstitials are either not ionized or they are compensated through defect association. The studies on the Cu/Ga stoichiometry indicate that the CuGaO_2 phase exhibits negligible equilibrium cation non-stoichiometry and thus the conductivity is invariant to *x*. This may contrast with non-equilibrium synthesis methods (thin film, etc.) in which it is possible to stabilize stoichiometric deviations which affect the conductivity, however the conductivity is typically of the same magnitude.

Future Plans:

Future work involves an investigation of co-doping in CuGaO_2 . Recent work has shown that co-doping is effective at inducing n- and p-type conductivity in ZnO . We will examine the effects of co-doping in CuGaO_2 through aliovalent ions such as Ni^{2+} and Sn^{4+} . In addition, an aerosol deposition system is being built to fabricate thick films directly from CuGaO_2 powders synthesized in our laboratory. This technique was originally developed by Akedo *et al.* for synthesis of Pb-based perovskites and other ceramic materials. In this technique, by using a pressure differential, submicron sized powders are ejected through a nozzle onto a substrate inside a vacuum controlled chamber. It is ideally suited for metastable materials such as CuGaO_2 because processing temperatures are generally limited to below 400°C.

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Education:

This work involves the collaboration of two graduate students (Meagen Marquardt, Nathan Ashmore), two undergraduate students (Ross Martin, Eric Patterson), a visiting scholar (Naratip Vittayakorn, Chiang-Mai University, Thailand), and an 8th grade science teacher (Christi Taylor). In addition, during summer semesters, the PI and graduate students have participated in ISU's Program for Women in Science and Engineering.



Christi Taylor (Waukee) demonstrates the measurement of pH for different solutions

Outreach:

With the collaboration of Christi Taylor, an 8th grade science teacher, the PI leads a summer science program for children aged 9-12 in Ames, IA. In Waukee, IA, the PI regularly visits Taylor's 8th grade science class to introduce students to the fundamental concepts of materials science and engineering.



The PI demonstrates heat treating of steel to 8th grade science students at Waukee Middle School, Waukee, IA.